

A Study of the Vapor Pressure of Aqueous Solutions of Cane Sugar at Twenty Degrees Centigrade

By

HUGH KLEMME PARKER

DISSERTATION

Submitted to the

Board of University Studies of the Johns Hopkins University
in Conformity with the Requirements for the
Degree of Doctor of Philosophy

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Acknowledgment

THE author desires to express his appreciation of the assistance, encouragement and inspiration given by Professors Frazer and Lovelace under whose direction this research was carried out.

To them, as well as to Professors Reid, Patrick, Morley and Doctor Thornton, the writer wishes to acknowledge a debt of gratitude for instruction in the lecture room and laboratory.

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BIOGRAPHY

THE VAPOR PRESSURE LOWERING OF AQUEOUS CANE SUGAR SOLUTIONS AT 20°

INTRODUCTION

The study of the vapor pressures of aqueous solutions of cane sugar offers an excellent opportunity for the correlation of colligative properties, especially so in the case of osmotic pressures since in both instances investigations can be carried out over a comparable wide range of concentrations. Though accurate vapor pressure measurements at the present stage of development are somewhat limited by temperature, it seems possible that they may also be extended over the temperature range covered by osmotic pressure. There is also the possibility of the experimental verification of the thermodynamic relation between osmotic pressure and vapor pressure lowering. Osmotic pressures calculated by the thermodynamic relations between colligative properties are in quite good agreement with the experimental data on the direct measurements by Morse¹, Frazer² and co-workers and Berkeley, Hartley and co-workers³.

The vapor pressure data for these particular solutions are not so numerous and have been measured in most cases by some dynamic method. Berkeley, Hartley and Burton⁴ measured the lowerings at 0° and claim an accuracy of 5% by their method. Washburn⁵ using a modified form of the apparatus of Berkeley and Hartley was able to obtain the values for a weight molar concentration at 25° which agreed well with the observed osmotic pressure values of Morse.

One of the first to observe vapor pressures of aqueous solutions by a static method using a Rayleigh manometer was Smits⁶, who worked with a NaNO_3 and NaCl solutions. Wood⁷ has measured the vapor pressures of concentrated sugar solutions at high temperatures by a static method. The static method has some decided advantages over the dynamic methods, which will not be enumerated at this time, except in regard to the fact that the general equation of Porter⁸ is derived on just such conditions as are encountered in the static method,

¹ Am. Chem. Journal, 45, 602 (1911).

² J. Am. Chem. Soc., 38, 1916 (1916).

³ Proc. Roy. Soc. A 206 486, (1906).

⁴ Proc. Roy. Soc. A 209 177, (1908).

⁵ J. Am. Chem. Soc., 37, 307 (1915).

⁶ Zeit phys. Chem., 51, 33 (1905).

⁷ Chem. News, 112, 91 (1915).

⁸ Proc. Roy. Soc., A77, 234 (1906).

namely; the solution is under the hydrostatic pressure of its own vapor.

Wood's method of static determination is limited to concentrated solutions and high temperatures where large differences of pressure occur, but for the precision necessary for the measurement at lower temperatures and concentrations, the static method of Frazer and Lovelace¹ is well adapted. The fact that the vapor pressure of the solution is compared directly with that of the pure solvent under exactly similar conditions and that the setting and reading error is within 0.0005 mm. actual lowering, leave little doubt as to the superiority of the method. Moreover, careful studies of the removal of dissolved air from the solutions by Rogers and Sease² have eliminated that source of error.

Measurements³ have been made on mannite by this method, and because of the fact that sugar shows all the properties of a hydrated non-electrolyte, and has been carefully investigated by various methods, including osmotic pressure, it seemed desirable to be able to compare the respective vapor pressure lowerings, as well as the osmotic pressures. For these reasons, and to be able to compare the osmotic pressures calculated by Porter's equation from statically determined vapor pressures with the direct measurements, sugar was chosen as the solute.

APPARATUS

The apparatus which had been standing idle for a period of about four years was thoroughly overhauled, cleaned with nitric acid and cleaning mixture, and finally steamed to remove any acid fumes that might remain. The mercury was redistilled and that required for the Rayleigh gauge, the McLeod gauge and the Thermoregulator was specially treated according to the method of Hulett⁴. During the war the Gaede pump which was originally used, had been removed and was replaced by a Langmuir mercury condensation pump in series with a General Electric auxiliary pump of large capacity. Between the auxiliary pump and the condensation pump was situated a small manometer, a stop cock to cut off between the two pumps, and a stop cock connected by a "T" in the line to a capillary for the purpose of relieving the vacuum either on the system or the Langmuir pump after closing Trap No. 1. A phosphorus pentoxide bulb was connected by a "T" and a ground glass joint in the glass just above the condensation pump to prevent water vapor being drawn into the oil of the

¹ J. Am. Chem. Soc., 36, 2439 (1914), Zeit phys. Chem., 89,155.

² Ibid., 43, 1793 (1920).

³ Loc. cit.

⁴ Phys. Rev., 33, 307.

auxiliary pump. With these exceptions the system used was that described by Lovelace, Frazer and Sease¹.

EXPERIMENTAL PROCEDURE

The sugar used was from the same source as that used in the osmotic pressure work here in this laboratory. It was not recrystallized, but showed a negligible amount of reducing sugar when tested with Fehling's solution (Allihn's method). Comparative analyses between it and a sample furnished by the Bureau of Standards on the saccharimeter and the interferometer revealed a presence of about .046% impurity in the solute used.

BUREAU OF STANDARDS NO. 17 SUGAR ANALYSIS

Moisture.....	less than 0.003%
Ash.....	less than .002%
Reducing substances estimated as invert sugar	
	less than .002%

In the preparation of solutions in vacuo, the same technique was followed as described by Sease and Rogers² in the case of dilute solutions. However, in the preparation of concentrated solutions, because of the great bulk of the sugar required, it was necessary to place the sugar in the larger bulb. The air was removed from the water in the small bulb by boiling cautiously with a smoky flame and sealing the constriction after about 30 minutes. The bulb containing the sugar was evacuated with the Langmuir pump for about an hour, at the end of which time the McLeod gauge showed negligible air pressure. The bulb was then sealed at the constriction. The bulbs containing air free sugar and air free water were joined at the stems by a short rubber tube from which the air had been displaced by distilled water and the latter by clean mercury, and which was wired into position by a double ligature at each end. The tips, which had been file marked before making the joint, were broken within the rubber connection and when the sugar had all dissolved the "introduction" bulb was completely filled with solution. By closing the rubber connection with a screw clamp, the larger bulb could be removed without exposing the solution to the air and the introduction capillary fitted in its place.

It was feared that the sugar might invert during the time required for the removal of air and the measurement of the vapor pressure, and thus increase the number of solute particles. Careful tests were made and it was found that in one case no inversion had occurred

¹ Loc. cit.

² Loc. cit.

over a period of 24 days. These tests were made by comparing the concentrations of the solutions as introduced against the concentrations taken out by the interferometer and by the saccharimeter.

TABLE I

0.1M	Stood 24 days	
	25.04°	Removed
	24.44°	Introduced
	= 1.0245 by saccharimeter	
0.0991M	Removed	
	= 1.0081 by interferometer	
	0.0983M	
	Introduced	
0.2M	Stood 20 days	
	50.197°	Removed
	50.01	Introduced
	= 1.0037 by saccharimeter	
0.1992	Removed	
	= 1.0045 by interferometer	
	0.1983	
	Introduced	
0.7M	Stood 8 days	
	79.475°	Removed
	76.86°	Introduced
	= 1.03402 by saccharimeter	
0.69599M	Removed	
	= 1.03408 by interferometer	
	0.67305M	
	Introduced	
5.0M	Stood 7 days	
	313.53°	Removed
	313.08	Introduced
	= 1.0014 by saccharimeter	
4.9815	Removed	
	= 1.0012 by interferometer	
	4.9755	
	Introduced	

The above ratios show that within the error of the saccharimeter reading, except in the case of the 0.1M, that the two methods check well enough to conclude that little or no inversion occurred.

The same criteria for determining when the solutions were air free as used by the other observers working on this method, were adopted and confirmed.

The analysis of the solutions was made by the interferometer after calibrating its sensitivity at the various concentrations. The known

solutions were carefully made up and the weighings corrected to vacuo. A little difficulty was encountered in reading the bands of the interferometer at the higher concentrations, due to the fact that they were more or less distorted and straighten only on long standing, which might involve some loss by evaporation. With some practice it was found that the readings could be checked satisfactorily after allowing 20 minutes for temperature differences to equalize, even though the bands were not straight.

Experimental Data

0.6960 MOLAR READINGS

Date	Zero Before	Reading	Zero After	Deflection
3/22/21	196.0	241.3	196.3	
	196.0	241.2	196.0	
	196.1	241.3	196.0	45.20
	195.6	240.7	195.5	
	195.5	240.8	195.6	
	195.6	240.8		45.20
3/2/21	195.7	240.9	196.0	
	196.0	241.0	196.0	
	196.0	241.1		
	196.0			45.04
	195.7	241.0	195.9	
	195.7	241.2	195.9	
	195.7	241.0		45.26
Mean of average deflection				45.17

0.6011 MOLAR READINGS

Date	Zero Before	Readings	Zero After	Deflection
3/21/21	195.7	235.0	196.0	
	196.0	235.1	196.0	
	196.0	235.0		
	196.0			39.07
	195.7	234.7	195.9	
	195.7	234.6	195.9	
	195.7	234.7		38.86
3/22/21	196.0	235.0	196.3	
	196.0	235.0	196.0	
	196.1	235.0	196.0	38.97
	195.6	234.5	195.5	
	195.5	234.6	195.6	
	195.6	234.6		39.00

With readings of 3/20/21, Average 38.95

0.4011 MOLAR READINGS

Date	Zero Before	Reading	Zero After	Deflection
1/24/21	249.95	275.06	250.06	25.06
1/24/21	249.13	274.10	249.13	24.97
1/24/21	249.93	275.00	250.03	25.02
1/24/21	249.11	274.13	249.16	25.02
1/31/21	247.86	273.03	247.96	25.12

Mean of average deflections 25.06

0.9937 MOLAR READINGS

Date	Zero Before	Reading	Zero After	Deflection
1/27/21	248.15	314.23	248.12	66.09
1/27/21	248.06	314.00	248.03	65.94
1/24/21	249.93	315.90	249.96	65.94
1/24/21	249.13	315.03	249.13	65.90
2/1/21	247.17	313.03	247.10	65.90
2/1/21	247.13	313.06	247.13	65.93

Mean of average deflections 65.95

0.0991 MOLAR READINGS

Date	Average Zero Before & After	Reading	Deflection
12/29/20	248.2	254.10	5.90
12/30/20	247.5	253.8	6.30
12/30/20	247.7	253.9	6.20

Mean of average 6.13

N.B.: These readings were chosen as best values because the average zeros before and after the reading checked within 0.1 mm. and both observers check.

Other readings on this concentration were discarded because of the inexperience of the observers and because zeros before and after, and readings themselves, did not check within 0.1 mm.

0.1992 MOLAR READINGS

Date	Average Zero Before & After	Reading	Deflection
12/30/20	247.3	259.7	12.40
12/30/20	247.6	259.8	12.20
Mean of average deflections			12.30

Note: These readings were chosen as best values because the average zeros before and after the reading checked within 0.1 mm.

Other readings on this concentration were discarded because of the inexperience of the observers and because either the zeros before and after or the readings themselves did not check within 0.1 mm.

2.0162 MOLAR READINGS

Date	Zero Before	Reading	Zero After	Deflection
3/1/21	246.4	392.1	246.3	145.70
	246.4	392.0	246.5	
	246.2	392.1	246.4	
	245.3	390.9	245.2	
	245.3	391.0	245.3	
	245.3	391.0		
2/27/21	246.1	392.1	246.2	145.69
	246.3	392.1	246.2	145.81
	246.3	392.0		
	246.2	392.0	246.5	
	246.3	392.3	246.2	
	246.5	392.2	246.3	145.84
	246.4			

With Readings of 2/26/21, Mean of average deflections 145.89

2.9916 MOLAR READINGS

Date	Zero Before	Reading	Zero After	Deflection
3/12/21	194.7	426.4	194.8	
	194.6	426.4	194.9	
	194.7	426.2	195.0	231.53
	194.0	425.9	194.2	
	194.2	425.9	194.1	
	194.0	425.9		231.8 ?
3/10/21	194.7	426.1	194.7	
	194.8	426.3	194.6	
		426.1	194.6	231.47
	194.0	425.4	194.0	
	194.0	425.5	193.9	
	194.0	425.4	193.9	231.47
Mean of average deflections				231.49

Question reading because temperature of bath dropped 0.1° of a degree.

4.0368 MOLAR READING

(Read against 2.9916M)

Date	I 4M Reading	II 2M Reading	III Average Zero	Deflection
2/27/21	430.33	392.03	246.21	
	430.03	392.18	246.34	
3/1/21	431.03	392.90	246.28	
	429.86	391.50	245.61	
	430.03	392.06	246.36	
	429.46	390.96	245.69	
2/26/21	430.73	393.26	247.21	
	430.03	393.30	247.18	
		Average 2M deflection		145.89
		Average 2M vs 4M deflection		183.72
		4 Molar deflection		329.61

N.B.: The 4 Molar deflection is obtained by subtracting the average of column III from the average of column I and adding this difference to that obtained by subtracting the average of column III from the average of column II. Maximum reading error 0.4% deviation from the mean.

4.9815 MOLAR READINGS

(Read against 2.9916M)

Date	I 5M Reading	II 3M Reading	III Average Zero	Deflection
3/10/21	386.96	426.16	194.69	
	386.03	425.43	193.96	
3/12/21	386.93	426.33	194.80	
	386.10	425.90	194.04	?
		Average 3M		231.49
		Average 5M vs 3M		192.16
		5M Deflection		423.65

Question reading because temperature of bath dropped 0.1° of a degree.

Method of determination of 5M deflection is the same as described for the 4M.

TABLE II

SUMMARY OF DATA

G = Grams of sugar per 1000 grams of H₂O (in vacuo)

M = Molar concentration

s = Deflection

k = Constant used in determination of lowering $\frac{d.}{D} = \frac{\sin \theta}{\frac{1}{2} \tan 2\theta}$ P₀ - P = Lowering at room temperature 25°

h = Lowering corrected to 0°

G	M	s	kx10 ⁻⁶	P ₀ - P	h
33.89	0.0991	6.13	5094	0.0312	0.0311
68.13	0.1992	12.30	5094	0.0627	0.0623
137.17	0.4011	25.05	5094	0.1276	0.1270
205.57	0.6011	38.95	5094	0.1984	0.1975
237.87	0.6960	45.17	5094	0.2301	0.2291
339.84	0.9937	65.95	5123	0.3379	0.3363
689.54	2.0162	145.89	5094	0.7432	0.7398
1023.13	2.9916	231.49	5069	1.1734	1.1681
1380.59	4.0368	145.89	5094	0.7432	
		183.72	5083	0.9339	1.6694
1703.67	4.9815	231.49	5069	1.1734	
		192.16	5074	0.9750	2.1387

TABLE III

DEVIATION FROM RAOULT'S LAW

M = Molar concentration

h = Lowering corrected to 0°

Calc. = Lowering calculated from Raoult's Law

 $\frac{P_0 - P}{M}$ = Molecular lowering

M	h	Calc.	Diff.	Mol Fraction x10 ⁻⁴	$\frac{P_0 - P}{n/N_{+n}}$	$\frac{P_0 - P}{M}$
0.0991	0.0311	0.0312	0.0001	17.8	17.466	0.3137
0.1992	0.0623	0.0627	0.0004	35.7	17.470	0.3131
0.4011	0.1270	0.1257	0.0013	71.6	17.740	0.3166
0.6011	0.1975	0.1877	0.0098	107.0	18.459	0.3285
0.6960	0.2291	0.2170	0.0121	123.7	18.622	0.3291
0.9937	0.3363	0.3082	0.0281	175.7	19.142	0.3384
2.0162	0.7398	0.6142	0.1256	350.2	21.124	0.3669
2.9916	1.1681	0.9118	0.2563	519.8	22.476	0.3904
4.0368	1.6694	1.1881	0.4813	677.3	24.647	0.4135
4.9815	2.1387	1.4433	0.6954	822.8	25.993	0.4293

DISCUSSION OF RESULTS

DEVIATION OF SUGAR SOLUTIONS FROM RAOULT'S LAW

The results tabulated in Table III show a marked divergence from the theoretical lowerings required by Raoult's law.

$$\frac{P_0 - P}{P_0} = \frac{n}{n + N} \text{ or } P = P_0 \frac{N}{n + N}$$

The differences between the calculated and observed values are recorded under the heading "Diff." and are expressed in millimeters of mercury. By plotting the values of the molecular lowering $\frac{P_0 - P}{M}$ against concentration of both sugar and mannite, it can be seen how the slope of the sugar curve, Figure 1, differs from the mannite. Because of the limited solubility of the mannite this curve must be extrapolated beyond one molar for comparison between a substance that obeys Raoult's law and one that does not. The theoretical molecular lowering curve is a straight line parallel to the concentration axis. The column of Table II headed, "Lowering Divided by the Mol Fraction," shows the calculated value for the vapor pressure of the pure solvent at 20° to the increase over the actual constant value which is 17.539 mm. of mercury according to Scheele and Heuse.

These abnormalities of vapor pressure lowering and other colligative properties of sugar solutions are usually explained by assuming that the solute forms hydrates in solution, or in other words, some of the

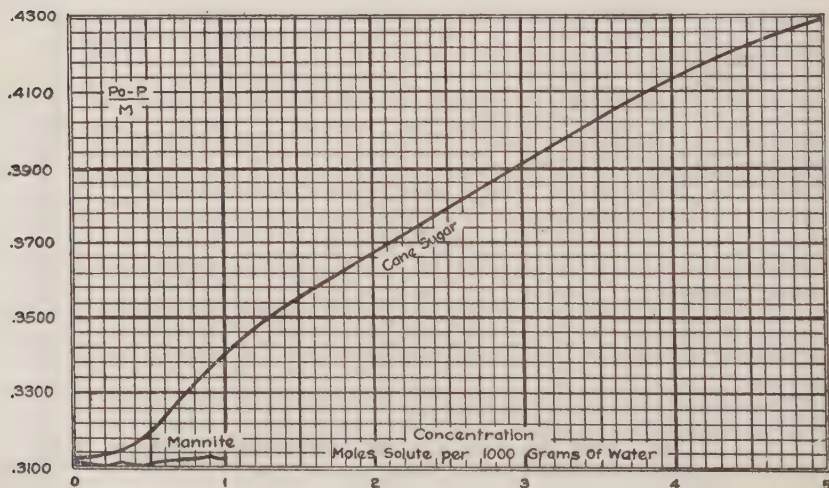


FIG. 1

water is held back in chemical combination with the sugar. Various investigators have calculated the amount of hydration of sugar. Callendar¹ obtains a value of five molecules of water combined with one molecule of sugar based on the boiling point determinations of Kahleberg². Washburn³ calculates from the freezing point data that sugar exists in solution as a hexahydrate. Findlay⁴ states, assuming water is not associated, and that the pressure of the solute has not altered the association of water, that the osmotic pressure calculated, assuming sugar to be a hexahydrate, is in almost exact agreement with Morse's observed value at 20° for a weight molar solution⁵. Wood⁶ calculates from static vapor pressure lowerings that sugar is a tetrahydrate at the higher temperatures and concentrations. Frazer & Myrick say that the degree of hydration varies with concentration and pressure and on the assumption that water is in the dihydrol form they obtain a tetrahydrate for 5M concentration by their osmotic pressure data at 30°. At 2, 3 and 4 molar concentrations they calculate that the pentahydrate exists.

Results calculated from the data of this research seem to indicate that sugar is a tetrahydrate in solution although they do not show the presence of a definite hydrate. Table IV is calculated from Raoult's law and assumes no association of the solvent.

TABLE IV

n = Mols of Sugar per 1000 grams H₂O (55.555 mols)
 N = Mols of Water calculated to represent active water (water with escaping tendency)
 H = Mols of Water calculated to be in combination with 1 mol of sugar at that particular concentration

n	N	H
0.0991	55.800	
0.1992	55.738	
0.4011	54.881	1.68
0.6011	52.681	4.76
0.6960	52.487	4.41
0.9937	51.038	4.45
2.0162	45.698	4.89
3.9916	41.592	4.67
4.0368	38.249	4.29
4.9815	35.617	4.00

¹ Proc. Roy. Soc., A, 80, 466 (1908).

² J. Physical Chem., 5, 362 (1901).

³ Technological Quarterly (M.I.T.) 31, 360 (1908).

⁴ "Osmotic Pressure" monograph, 42.

⁵ Loc. cit.

⁶ Loc. cit.

⁷ Loc. cit.

The degree of combination between sugar and water is difficult to determine because of the fact that water is known to be associated, and the effect of the presence of a solute on association and especially the effect of the presence of a hydrated solute is not known. An interesting parallel phenomenon is observed in that simultaneously with the retaining of active water by the sugar, there is a diminution of volume in the preparation of solutions. A solution of cane sugar in water does not occupy as large a volume as would be expected from molecular volume considerations. In other words the solution is made up of components that are not truly additive. Bousfield and Lowry and Richards postulate that the more voluminous constituent of the ternary mixture of water has been removed or has been acted upon as the case may be. If there is hydrate formation the active water is partially changed into hydrate water, the volume changes and the vapor pressure, which is the measure of active water, relatively diminishes, and thus it seems that the shrinkage of volume on dissolution substantiates the theory of hydrates of sugar in solution.

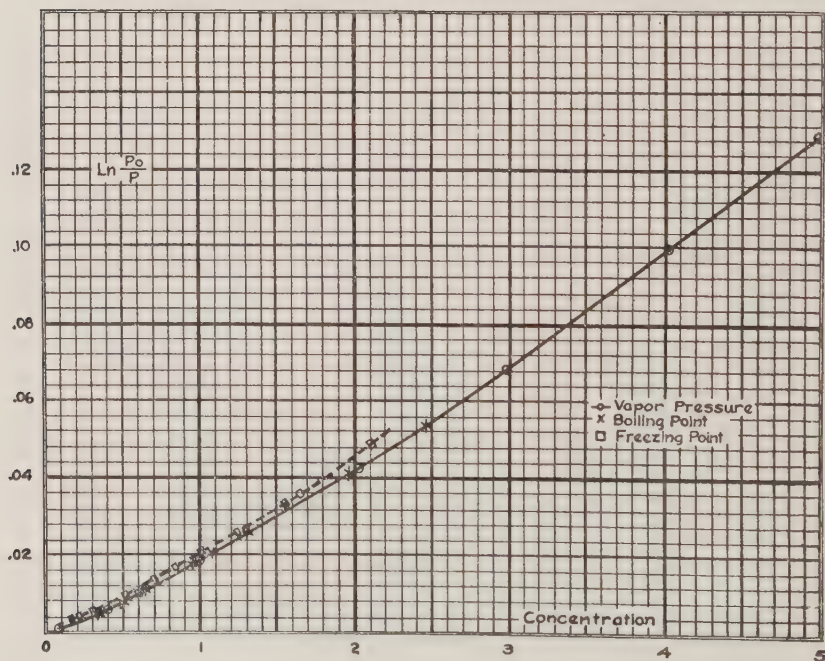


FIG. 2

DEVIATION FROM VON BABO'S LAW

The temperature coefficient of vapor pressure of sugar solutions is of interest since it affords a means of comparison with the observed osmotic pressure temperature coefficient. Von Babo's law states that the relative vapor pressure lowerings are independent of the temperature, that is, $\frac{d(\ln P_0/p)}{dT} = 0$. It is obvious from Figure 11 that such conditions do not exist for sugar solutions, even though in the absence of vapor pressure measurements at other temperatures it was necessary to resort to the indirect method by using the freezing point and boiling point calculations given by Jüttner¹. These values are chosen from the work of Beckman² on boiling points and Ewan³ on freezing points. Although it is a little difficult to know and chose the best values which represent the true state of affairs, it appears that the curve for the freezing point lies above that of the vapor pressure, and the curve for the boiling point lies below. The Kirchhoff equation $H = RT^2 \frac{\partial}{\partial T} \left(\frac{\ln P_0}{P} \right)$ where H = the heat of dilution and the other symbols have their usual meaning, accounts quantitatively for this deviation. "H" is defined as the heat which must be added to keep the temperature constant when one gram of solvent is added to an infinite amount of solution. Calculations based on Ewan's⁴ freezing point data and this 20° vapor pressure work show the heat of dilution to be greater than that observed by Ewan and Stackelberg⁵.

TABLE V

H EXPRESSED AS CALORIES PER GRAM AT 1.0M

H Ewan	H Stackelberg	H calc.
-.203	-.309	-.402
at 2.0M		
-.43		-.79

An explanation for the divergence can be found in the fact that the calculated values are based on interpolated values and that the freezing point data may not be a reliable starting point for the lower limit of the integral.

Because of the accuracy of the vapor pressure method it is believed that heats of dilution can be accurately determined for the higher concentrations, assuming of course, the validity of Kirckhoff's equation.

¹ Zeit physik. Chem., 38, 106 (1901).² Ibid., 6, 437 (1890).³ Ibid., 31, 82 (1899).⁴ Loc. cit.⁵ Zeit phys. Chem., 30, 546 (1898).

OSMOTIC PRESSURE AND VAPOR PRESSURE LOWERING

For the thermodynamic relation between vapor pressure and osmotic pressure, the equation derived by Porter¹ is better adapted for the calculation of osmotic pressures from this data than that of Lewis². The equation of Lewis is intended to apply to ideal solutions, while Porter's expression can be applied in general. Moreover, Porter's equation is based upon the fact that the solution is under the hydrostatic pressure of its own vapor which is a condition of this static method of vapor pressure determination.

USING PORTER'S NOTATION WHERE

P_p = osmotic pressure under hydrostatic pressure p

p = hydrostatic pressure

π_π = vapor pressure of solution when under hydrostatic pressure of its own vapor

π_0 = vapor pressure of solvent when under hydrostatic pressure of its own vapor

s = Reduction in volume when 1 gram of solvent escapes

v = specific volume of vapor

u = specific volume of solvent

the relation is expressed by the equation:

$$\int_{\pi_\pi}^p \frac{p}{s} dp = \int_{\pi_0}^{\pi_\pi} \frac{\pi_\pi}{v} d\pi + \int_{\pi_\pi}^p \frac{p - P_p}{u} dp \quad (1)$$

Assuming s and u to be independent and that the vapor obeys the gas laws the integrated form, when simplified and terms disregarded that may be neglected, becomes:

$$P - \frac{aP^2}{2} = \frac{RT}{V_s} \ln \frac{P_0}{P} \quad (2)$$

where P = the osmotic pressure

a = compressibility coefficient

V_s = diminution in volume where 1 gram of solvent is taken from an infinite amount of solution

R = gas constant

T = absolute temperature

$\ln \frac{P_0}{P}$ = values obtained from vapor pressure data --for vapor pressure solution (P) and solvent (P_0)

The V_s value may be obtained from the equation of Gouy and Chaperon¹,

$$V_s = \frac{1}{\delta} \left(1 + \frac{s}{\delta} \frac{\partial \delta}{\partial s} \right)$$

where δ = density of the solution
 s = wt of solute in 1 gram of solution

CALCULATED OSMOTIC PRESSURES OF CONCENTRATED SOLUTIONS BY PORTER'S EQUATION

In the calculation of the following values the universal gas constant was used and no correction was applied to the 1M or 2M concentrations for compressibility—that data of Plato in Landolt Börnstein Tabellen was used for the density of sugar solutions.

TABLE VI

M	d	V_s	P calc.	P'obs	P''obs	P'''obs
0.9937	1.1054	1.0008	25.88	26.64		
2.0162	1.1795	0.998	56.50	56.70	57.7	54.9
2.9916	1.2337	0.990	93.08	92.80	91.5	95.1
4.0368	1.2747	0.989	135.27	138.20	133.5	136.2
4.9815	1.3103	0.983	177.19	187.20	179.8	

P'obs = Lotz's¹ values corrected for temperature from 30° measurements except 1M which is value given by Morse

P''obs = Frazer and Myrick's values corrected for temperature from 30° measurements

P'''obs = Berkeley and Hartleys' values corrected for temperature from 0° measurements

The agreement between the calculated and the observed is quite good except in the case of the 5M where a difference of 5.6% occurs between the calculated value and that observed by Lotz with the water interferometer pressure gauge. Only in one concentration, 3M, is the calculated value higher than the observed. The correction of the observed pressures for temperatures is somewhat doubtful because the temperature coefficient of osmotic pressures at those concentrations

¹ Ann Chim phys. (6) 12, 384 (1887).

² Lotz dissertation, J. H. U., 1920.

is not known. The agreement between Frazer and Myrick's¹ values and Berkeley and Hartley's² 0° values when corrected by assuming that the solutions obey the gas law, is good, considering the range of temperature, and for this reason the same method of correction of observed values was used in table VI. If heats of dilution data were available at these temperatures and concentrations perhaps that method of correction would bring the calculated and observed values nearer together. In support of this supposition take the case of the

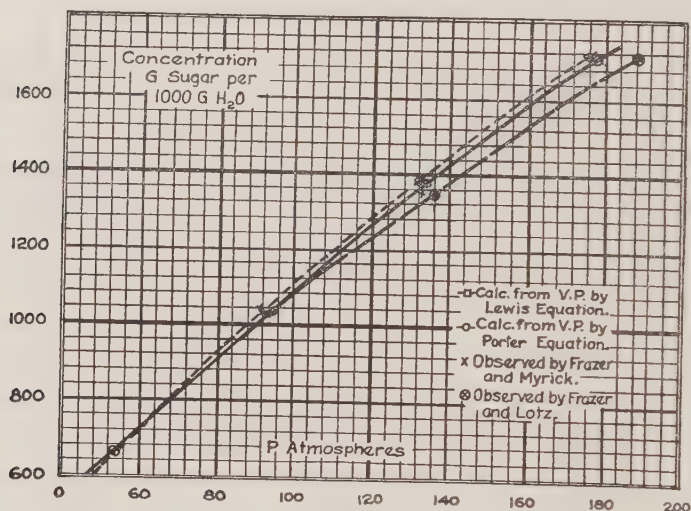


FIG. 3

2M solution where Ewan's data can be used. The application of the Helmholtz equation according to Lewis corrects the observed value so that it nearly checks the calculated value, thus:

$$P - Q = T \frac{dp}{dt}$$

Q = heat of dilution, .43 calories according to Ewan

.43 cal. $\approx$ 18 cc. atmospheres

58 = value of P at 30° according to Lotz

$$\frac{58 - 18}{293} = .13 \text{ atmospheres per degree}$$

$$.13 \times 10 = 1.3$$

$$58 - 1.3 = 56.7 \text{ atmospheres pressure at } 20^\circ$$

56.5 calculated from vapor pressure

¹ Loc. cit.

² Loc. cit.

OSMOTIC PRESSURES OF CONCENTRATED SOLUTIONS CALCULATED BY LEWIS' EQUATION

The equation of Lewis is given as follows:

$$\Pi - \frac{1}{2}a\Pi^2 = \frac{RT}{V_0} \ln \frac{P_0}{P} \quad (3)$$

where a = compressibility

Π = osmotic pressure

V_0 = molecular volume of the solvent and the other symbols have their usual meaning.

The values calculated from this equation compared with those calculated by Porter's equation are set down in Table VII. It is evident from an examination of the table and the curve, Figure 3, that the values by equation (3) are higher at the low concentrations and lower at the high concentrations than those of equation (2), in other words, the curves intersect at about 3M concentration.

TABLE VII

Molar Conc.	Calculated by Equation 3	Calculated by Equation 2
1	25.91	25.88
2	57.60	56.50
3	92.16	93.08
4	133.86	135.37
5	174.29	177.19

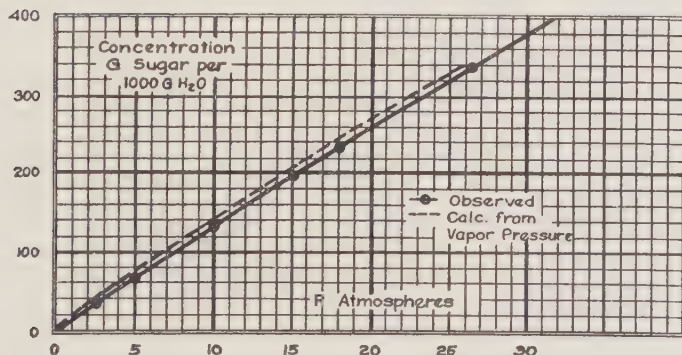


FIG. 4

THE CALCULATED OSMOTIC PRESSURES OF DILUTE SOLUTIONS

The calculation of the osmotic pressures recorded in Table VIII was done with equation (3) and compressibility neglected. These calculated values are lower than the observed values by about 0.2 of an atmosphere at the lower concentrations and about 0.5 of an atmosphere at the higher. The discrepancy is difficult to explain, but a similar deviation in the same direction was observed by Rogers¹ when comparing the calculated values with the direct measurements of osmotic pressure. There is a possibility that the manometer measured too high a pressure because of air being trapped between the glass and the mercury as the mercury thread ascended. Further suspicion is cast upon the manometer as a pressure indicator from the fact that at the higher pressures a calibration of a manometer against the water interferometer pressure gauge (which had been in turn calibrated against the absolute gauge at the Geophysical laboratory) revealed a difference between the two gauges of just about the amount necessary to account for the difference between the observed and calculated osmotic pressures. However it is not safe to say that the manometer is the source of divergence until further study has been made.

Both the equation of Lewis and that of Porter are based on the assumption that water vapor obeys the gas law. In view of the fact that there are known deviations from the gas law, this point is well worth considering, though, of course, experimental evidence seems to show the divergences most marked at the higher pressures while this work is carried out under 17 mm. of mercury pressure just where little or no abnormality should be shown. Batelli gives a variation in PV for water vapor at 21° of only 0.1% over a range of 10 millimeters pressure. In these vapor pressure measurements of sugar solutions it must be remembered that the vapor is saturated; and consequently at this slight pressure of 17 mm. since the experimental error in the measurement of PV of the unsaturated vapor is quite appreciable as Lord Rayleigh has observed, the error must be magnified in the case of saturated vapor; and thus the data are difficult to credit one way or the other. Further study of the deviations of water vapor from the gas law at low pressures may reveal facts that will account for the difference noted above.

¹ Rogers' Dissertation, J. H. U., 1917.

TABLE VIII

COMPARISON OF MEASUREMENTS OF OSMOTIC PRESSURES OF DILUTE SOLUTIONS OF MANNITE AND SUGAR BY DIRECT AND INDIRECT METHODS¹

Molar conc	Mannite		Sugar	
	obs	calc	obs	calc
0.1		2.327	2.59	2.37
0.2	4.86	4.68	5.06	4.70
0.4	9.59	9.39	10.13	9.68
0.6	14.40	14.24	15.39	15.15
0.7		16.53	18.13	17.61
1.0	24.12	23.75	26.64	25.91

TABLE IX

SUMMARY OF CALCULATED AND OBSERVED OSMOTIC PRESSURES

G. Sugar per 1000g of water Morse, Myrick & Frazer Lotz	G. Sugar per 1000g of water Vapor Pressure Measurements	Observed by Morse & co-workers	Observed by Frazer & Myrick	Observed by Frazer & Lotz	Calculated by Lewis' Equation	Calculated by Porter's Equation
33.91	33.89	2.59			2.37	
67.82	68.13	5.06			4.70	
135.64	137.17	10.13			9.68	
203.46	205.57	15.35			15.15	
237.37	237.89	18.13			17.61	
339.1	339.84	26.64			25.91	25.88
684.4	689.54		57.7*	56.7*	57.60	56.5
1026.6	1023.13		91.5**	92.8**	92.19	93.08
1368.8	1380.59		133.5**	138.2**	133.86	135.37
1711.0	1703.67		179.8**	187.2**	174.29	177.19

SUMMARY

1. The vapor pressures of aqueous sugar solutions over the range of solubility at 20° have been measured.

2. The deviations of sugar solutions from Raoult's law have been recorded and discussed.

3. It has been shown that von Babo's law does not hold for sugar solutions.

4. Osmotic pressures have been calculated both for concentrated and dilute solutions by the equations of Lewis and Porter and compared with the observed values at this temperature.

* Corrected for temperature from 30° measurements by heat of dilution.

** Corrected for temperature from 30° measurements by gas law.

BIOGRAPHY

HUGH Klemme Parker was born in Iowa, April 11, 1894. He received his early education in the Public Schools of Fayette, Iowa. He was graduated from Upper Iowa University with a Bachelor of Arts degree in 1916. After teaching the scholastic year 1916-1917 in West Union Iowa High School, he entered the University of Chicago to begin graduate work. During the war he served in the Chemical Warfare Service. After his discharge from the army, he was Carnegie research assistant to Prof. Frazer of Johns Hopkins University. He entered Johns Hopkins University as a graduate student in chemistry, January 1, 1920. Physical Chemistry and Mathematics were his subordinate subjects. During the years 1919-20 and 1920-21 he was appointed University Scholar.

